

# Exam II, Sunday April 19

3:00 - 4:20 PM  
Chapters 16.7 - 20.1

Hill-114, Secs 08,16,18  
ARC-103, Secs 01,03,12,14  
SEC-111, Secs 04,15

You must take the exam at your assigned location.

# Review Chapters 16, 17, 18, 19, 20

## Topics

1. Chapter 16.7 Reaction Mechanisms
2. Chapter 17
  1. Equilibrium expressions
3. Chapter 18
  1. Acids and bases
4. Chapter 19
  1. Salts, buffers, and acid-base titrations products.
  2. Solubility product  $K$
5. Chapter 20
  1. Entropy

## Chapter 16.

→ Mechanisms

→ Catalyst

## **The Rate-Determining Step of a Reaction Mechanism**

The overall rate of a reaction is related to the rate of the slowest, or rate-determining step.

## **Correlating the Mechanism with the Rate Law**

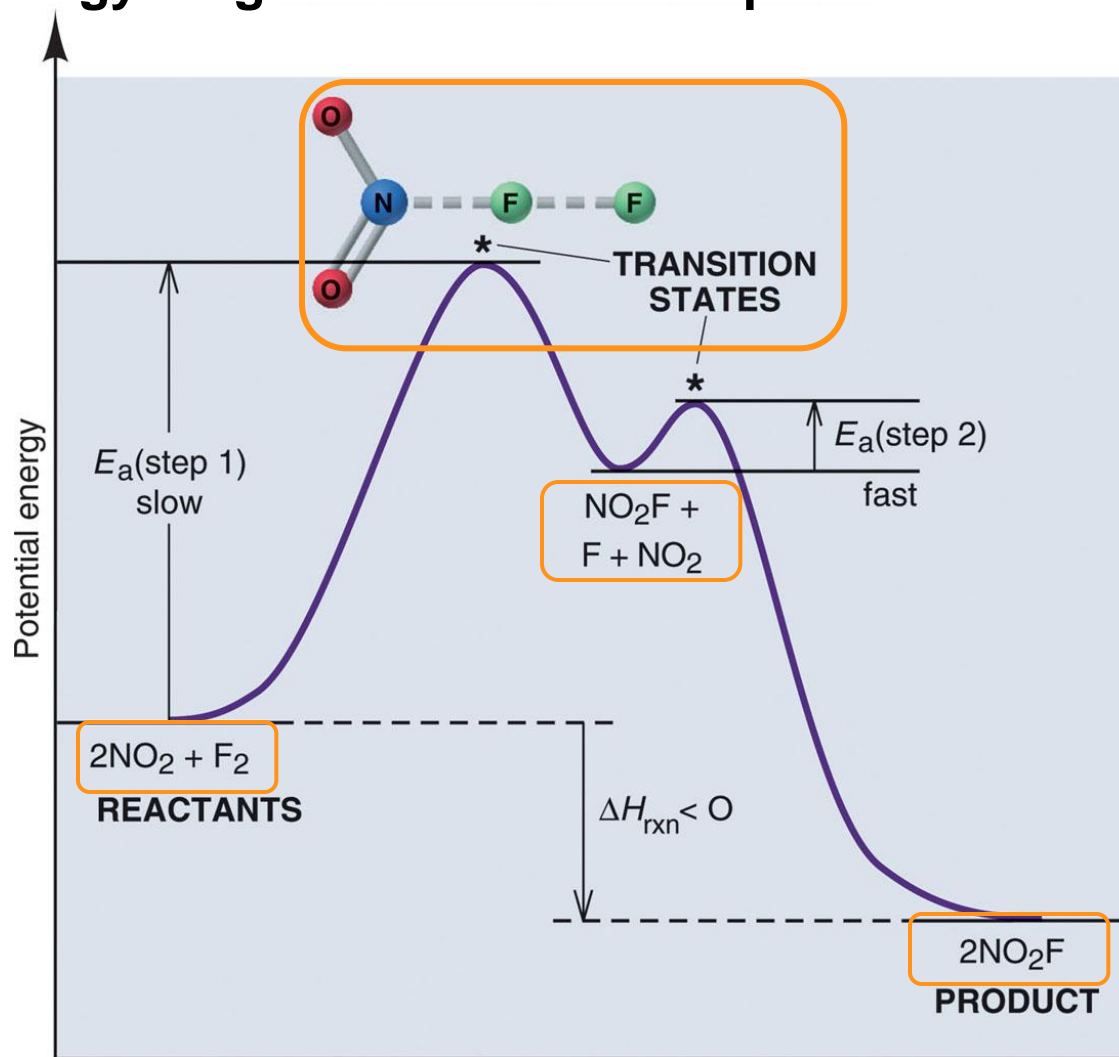
The elementary steps must add up to the overall equation.

The elementary steps must be physically reasonable.

The mechanism must correlated with the rate law.

Figure 16.18

Reaction energy diagram for the two-step reaction of  $\text{NO}_2$  and  $\text{F}_2$ .

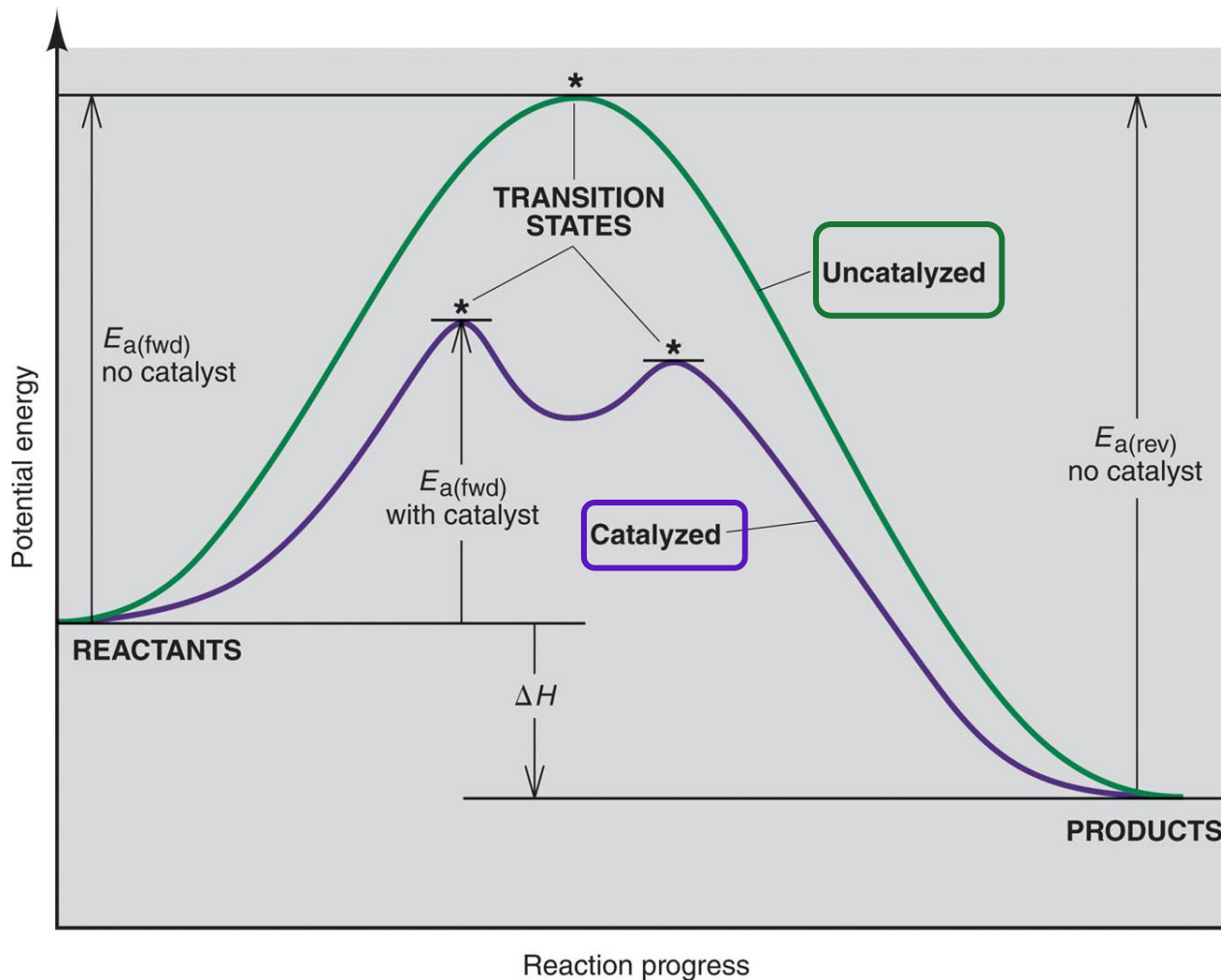


# CATALYSTS

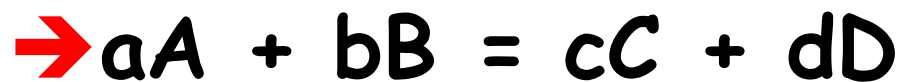
- Each catalyst has its own specific way of functioning.
- In general a catalyst lowers the energy of activation.
- Lowering the  $E_a$  increases the rate constant,  $k$ , and thereby increases the rate of the reaction
- A catalyst increases the rate of the *forward* AND the *reverse* reactions.
- A catalyzed reaction yields the products more quickly, but **does not yield more product** than the uncatalyzed reaction.
- A catalyst lowers  $E_a$  by providing a different mechanism, for the reaction through a new, lower energy pathway.

Figure 16.19

Reaction energy diagram of a catalyzed and an uncatalyzed process.



## Writing rate laws



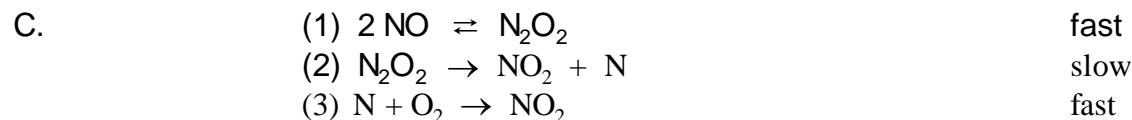
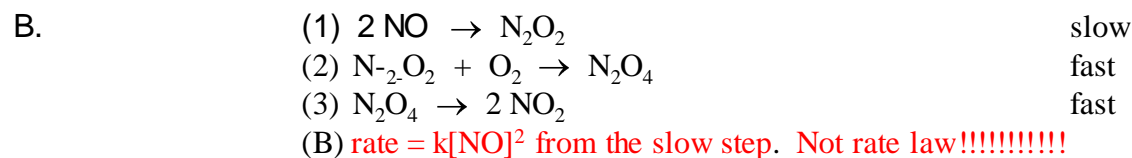
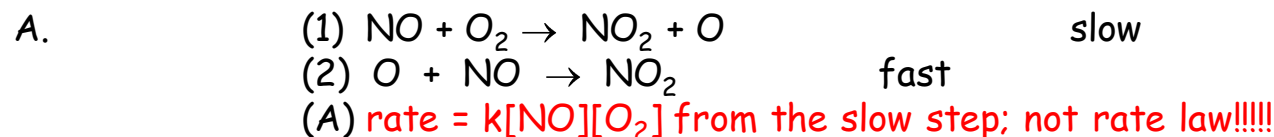
→  $\text{rate (forward)} = k_1[A]^a[B]^b$

→  $\text{rate (reverse)} = k_{-1}[C]^c[D]^d$

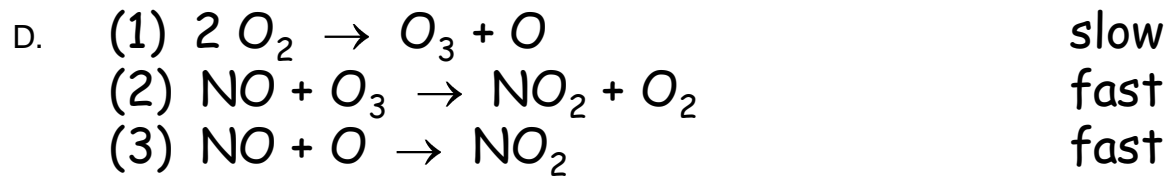


The reaction  $2 \text{NO} + \text{O}_2 \rightarrow 2 \text{NO}_2$  exhibits the rate law:  $\text{rate} = k [\text{NO}]^2 [\text{O}_2]$ . Which one of the following five mechanisms is consistent with this rate law?

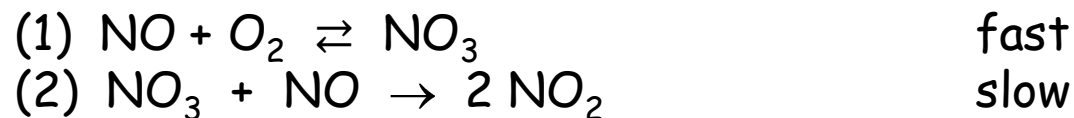
**Note: If first step is slow, this will be the rate law.**



(C)  $\text{rate} = k_2[\text{N}_2\text{O}_2]$  from the slow step,  
 but this is not the final expression, since  $\text{N}_2\text{O}_2$  is an intermediate.  
 Use step (1) and set the rate of the forward reaction equal to the rate of the reverse reaction. Then  
 $k_1[\text{NO}]^2 = k_{-1}[\text{N}_2\text{O}_2]$ . Solving for  $[\text{N}_2\text{O}_2]$  and substituting into  
 $\text{rate} = k_2[\text{N}_2\text{O}_2]$  gives  $\text{rate} = (k_2 k_1 / k_{-1})[\text{NO}]^2$ , which may be written as  $\text{rate} = k[\text{NO}]^2$ . **not rate law!!!!**



(D) rate =  $k[\text{O}_2]^2$  from the slow step



$$\text{rate} = k_2[\text{NO}_3][\text{NO}],$$

where  $[\text{NO}_3]$  is an intermediate. Using step (1) gives

$$k_1[\text{NO}][\text{O}_2] = k_{-1}[\text{NO}_3],$$

$$[\text{NO}_3] = (k_1/k_{-1}) [\text{NO}][\text{O}_2]$$

Substitution of  $[\text{NO}_3]$  into  
slow (2) rate =  $k_2[\text{NO}_3][\text{NO}]$ , gives

$$\text{rate} = k_2 k_1/k_{-1} [\text{NO}][\text{O}_2][\text{NO}]$$

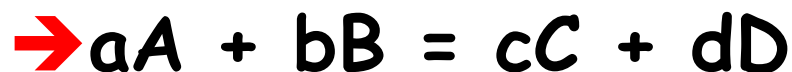
and then rate =  $(k_2 k_1/k_{-1})[\text{NO}]^2[\text{O}_2]$ , or rate =  $k[\text{NO}]^2[\text{O}_2]$ .

Therefore, the answer is **E**.

# Chapter 17

## The Extent of Chemical reaction

## Writing $Q_c$



$$Q_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

→ Call this  $Q_c$  reaction quotient i.e. **reaction status**.

→ Be sure that the equation is balanced!!!  
Solids do not appear in the expressions!!!!

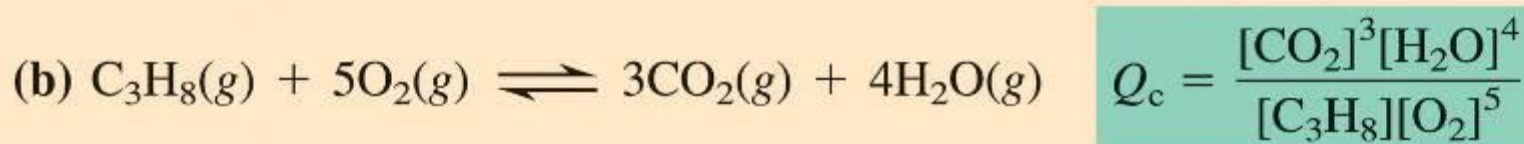
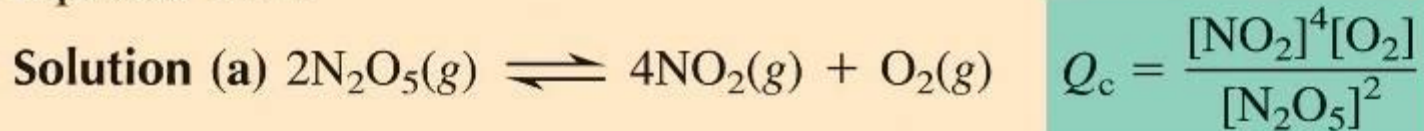
## SAMPLE PROBLEM 17.1 Writing the Reaction Quotient from the Balanced Equation

**Problem** Write the reaction quotient,  $Q_c$ , for each of the following reactions:

(a) The decomposition of dinitrogen pentaoxide,  $\text{N}_2\text{O}_5(g) \rightleftharpoons \text{NO}_2(g) + \text{O}_2(g)$

(b) The combustion of propane gas,  $\text{C}_3\text{H}_8(g) + \text{O}_2(g) \rightleftharpoons \text{CO}_2(g) + \text{H}_2\text{O}(g)$

**Plan** We balance the equations and then construct the reaction quotient as described by Equation 17.4.



**Check** Always be sure that the exponents in  $Q$  are the same as the balancing coefficients. A good check is to reverse the process: turn the numerator into products and the denominator into reactants and change the exponents to coefficients.

## Writing $Q_c$ for multistep

- When you have a multi step reaction, the final value of  $Q_c$  will be obtained by adding the different reactions together and thus you have to multiply the  $Q$ 's.
- $Q_{c \text{ overall}} = Q_1 \times Q_2 \times Q_3 \times \dots$
- This also means that
- $K_{\text{overall}} = K_1 \times K_2 \times K_3 \times \dots$

## Example 1

- $\text{C(s)} + (1/2) \text{O}_2(\text{g}) \rightleftharpoons \text{CO(g)} \quad K_1$
- $\text{CO(g)} + (1/2) \text{O}_2(\text{g}) \rightleftharpoons \text{CO}_2(\text{g}) \quad K_2$
- Need
- $2 \text{CO(g)} \rightleftharpoons \text{C(s)} + \text{CO}_2(\text{g})$
- Re-write:
- $\text{CO(g)} + (1/2) \text{O}_2(\text{g}) \rightleftharpoons \text{CO}_2(\text{g}) \quad K_2$
- $\text{CO(g)} \rightleftharpoons \text{C(s)} + (1/2) \text{O}_2(\text{g}) \quad 1/K_1$
- Add up: (same as multiplying equilibrium constant)
- $2\text{CO(g)} \rightleftharpoons \text{C(s)} + \text{CO}_2(\text{g})$
- $K_{\text{overall}} = K_2/K_1$



## Equilibria with pressure

→  $PV = nRT$ ,  $P = nRT/V$  or  $P/RT = n/V$

→  $2\text{NO}(g) + \text{O}_2(g) = 2\text{NO}_2(g)$

→ Balanced equation is most important.

$$Q_p = \frac{p_{\text{NO}_2}^2}{p_{\text{NO}}^2 p_{\text{O}_2}}$$

$$K_p = K_c (RT)^{\Delta n_{\text{gas}}}; \text{ when } \Delta n_{\text{gas}} = 0; K_p = K_c$$

## Example 6

How much carbon is produced?

→ Start concentration =  $1.5 \text{ mole}/2.00 \text{ L} = 0.75\text{M}$

→  $\text{CS}_2(\text{g}) = \text{C}(\text{s}) + \text{S}_2(\text{g})$

→ Initial            0.75            0            0

→ Change            -x            x            x

→ Equil            0.75-x            x            x

→  $x/(.75-x) = 0.179$ ;  $x = 0.114\text{M}$ ;

→  $(0.114 \text{ mole/L}) \cdot (2\text{L}) \cdot (12.01\text{g/mole}) = 2.74 \text{ g C(s)}$

→ Note that  $\text{C}(\text{s})$  is not in the equilibrium expression,

→  $x^2/(.75-x) = 0.179$  (WRONG)

## Example 4

- $\text{CO(g)} + \text{H}_2\text{O(g)} \rightleftharpoons \text{CO}_2\text{(g)} + \text{H}_2\text{(g)}$
- Initial .1                      .1                      .4                      .4
- Use moles because  $\Delta n = 0$ .
- Find  $Q_c = (.4)^2 / (.1)^2 = 16 > K_c = 4$ ; This means that reaction goes to the left because you passed equilibrium
- $\text{CO(g)} + \text{H}_2\text{O(g)} \rightleftharpoons \text{CO}_2\text{(g)} + \text{H}_2\text{(g)}$
- Change .1+x                      .1+x                      .4-x                      .4-x
- $x = 0.0667$

## Problem 2

- For which reaction will  $K_p = K_c$ ?
- A.  $\text{CH}_4(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CO}(\text{g}) + 3 \text{H}_2(\text{g})$
- B.  $\text{C}(\text{s}) + \text{CO}_2(\text{g}) \rightleftharpoons 2\text{CO}(\text{g})$
- C.  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2 \text{NH}_3(\text{g})$
- D.  $\text{CO}(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CO}_2(\text{g}) + \text{H}_2(\text{g})$  ←
- E.  $\text{NH}_4\text{HS}(\text{s}) \rightleftharpoons \text{NH}_3(\text{g}) + \text{H}_2\text{S}(\text{g})$
- Need  $\Delta n_{\text{gas}} = 0$ ;
- $K_p = K_c (RT)^{\Delta n_{\text{gas}}}$

## Reaction Directions

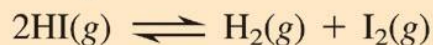
- If  $Q < K$ , favor products
- If  $Q > K$ , favor reactants
- If  $Q = K$ , in equilibrium.

# Equilibrium Calculations

- Always start with balanced equation with state signs i.e. g, l, or s.
- Use a table to account for all the reactants and products.
- What are the **I**nitial concentrations?
- Do the **C**hanges,
- Add the columns,
- Then get **E**quilibrium quantities,
- Solve for  $x$ .

**SAMPLE PROBLEM****Calculating  $K_c$  from Concentration Data**

**Problem** In a study of hydrogen halide decomposition, a researcher fills an evacuated 2.00-L flask with 0.200 mol of HI gas and allows the reaction to proceed at 453°C:



At equilibrium,  $[\text{HI}] = 0.078\text{ M}$ . Calculate  $K_c$ .

**Plan** To calculate  $K_c$ , we need the equilibrium concentrations. We can find the initial  $[\text{HI}]$  from the amount (0.200 mol) and the flask volume (2.00 L), and we are given  $[\text{HI}]$  at equilibrium (0.078 M). From the balanced equation, when  $2x$  mol of HI reacts,  $x$  mol of  $\text{H}_2$  and  $x$  mol of  $\text{I}_2$  form. We set up a reaction table, use the known  $[\text{HI}]$  at equilibrium to solve for  $x$  (the  $[\text{H}_2]$  or  $[\text{I}_2]$  that forms), and substitute the concentrations into  $Q_c$ .

**Solution** Calculating initial  $[\text{HI}]$ :

$$[\text{HI}] = \frac{0.200\text{ mol}}{2.00\text{ L}} = 0.100\text{ M}$$

Setting up the reaction table, with  $x = [\text{H}_2]$  and  $[\text{I}_2]$  that form and  $2x = [\text{HI}]$  that reacts:

Concentration (M)	$2\text{HI}(g)$	$\rightleftharpoons$	$\text{H}_2(g)$	+	$\text{I}_2(g)$
Initial	0.100		0		0
Change	$-2x$		$+x$		$+x$
Equilibrium	$0.100 - 2x$		$x$		$x$

Always use the stoichiometric value for the change.

Solving for  $x$ , using the known  $[\text{HI}]$  at equilibrium:

$$[\text{HI}] = 0.100\text{ M} - 2x = 0.078\text{ M}$$

$$x = 0.011\text{ M}$$

Therefore, the equilibrium concentrations are

$$[\text{H}_2] = [\text{I}_2] = 0.011\text{ M} \quad \text{and} \quad [\text{HI}] = 0.078\text{ M}$$

Substituting into the reaction quotient:

$$Q_c = \frac{[\text{H}_2][\text{I}_2]}{[\text{HI}]^2}$$

Thus,

$$K_c = \frac{(0.011)(0.011)}{0.078^2} = 0.020$$

**Check** Rounding gives  $\sim 0.01^2/0.08^2 = 0.02$ . Because the initial  $[\text{HI}]$  of  $0.100\text{ M}$  fell slightly at equilibrium to  $0.078\text{ M}$ , relatively little product formed; so we expect  $K_c < 1$ .

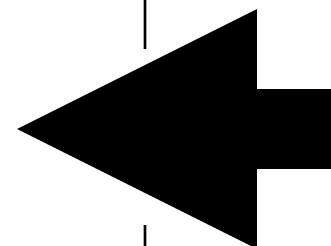


# Le Chatelier's Principle

- Effects of the equilibrium when:
  - ★ Adding more heat to an exothermic ( $-\Delta H$ )
  - ★ Adding more heat to an endothermic ( $\Delta H$ )
- Adding more gas molecules?
- Increasing or decreasing the pressure?
- All these will change the direction of the reaction depending on which side of the reaction the changes occur.
- When a disturbance occurs, the equilibrium position will shift and the concentrations (or pressures) change in a way that reduces the disturbances and the system attains a new equilibrium. ( $Q = K$  again).

**Table 17.4** Effect of Various Disturbances on an Equilibrium System

Disturbance	Net Direction of Reaction	Effect on Value of $K$
Concentration		
Increase [reactant]	Toward formation of product	None
Decrease [reactant]	Toward formation of reactant	None
Increase [product]	Toward formation of reactant	None
Decrease [product]	Toward formation of product	None
Pressure		
Increase $P$ (decrease $V$ )	Toward formation of fewer moles of gas	None
Decrease $P$ (increase $V$ )	Toward formation of more moles of gas	None
Increase $P$ (add inert gas, no change in $V$ )	None; concentrations unchanged	None
Temperature		
Increase $T$	Toward absorption of heat	Increases if $\Delta H_{\text{rxn}}^0 > 0$ Decreases if $\Delta H_{\text{rxn}}^0 < 0$
Decrease $T$	Toward release of heat	Increases if $\Delta H_{\text{rxn}}^0 < 0$ Decreases if $\Delta H_{\text{rxn}}^0 > 0$
Catalyst added	None; forward and reverse equilibrium attained sooner; rates increase equally	None



# Chapter 18 Acid-Base Equilibria

→ pH scale:  $\text{pH} = -\log[\text{H}_3\text{O}^+]$ ;

★  $\text{pH} + \text{pOH} = 14$ .

→ Definition of an acid: Proton donor

→ Acid Strength

★ Know strong acids ( $\text{HNO}_3$ ,  $\text{HCl}$ , etc)

★ Acid strength down period table and number of Os.

→ Strong Bases

★  $\text{NaOH}$ ,  $\text{KOH}$  (Alkaline and alkali earth hydroxides)

→ Weak Bases

★  $\text{NH}_3$ , organic amine bases

## Example 5.

- Given the following data, calculate the enthalpy of the autoionization of water.
- At 25°C,  $K_w = 1.0 \times 10^{-14}$  ; and at 60°C,  $K_w = 1.0 \times 10^{-13}$  (note difference).
- Note that pH of pure water at 60° is 6.5.

$$\ln \frac{K_{w2}}{K_{w1}} = -\frac{\Delta H^0}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\rightarrow \Delta H^0 = 54.3 \text{ kJ}$$

## 18.6 Molecular properties and acid strength

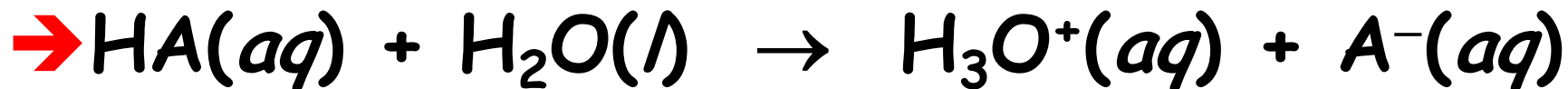
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Electronegativity increases,  
acidity increases

Bond strength decreases,  
acidity increases

6A(16)	7A(17)
H <sub>2</sub> O	HF
H <sub>2</sub> S	HCl
H <sub>2</sub> Se	HBr
H <sub>2</sub> Te	HI

## Acid Dissociation Constant ( $K_a$ )

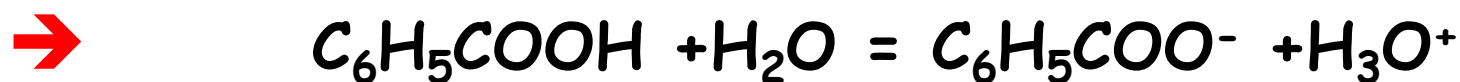


$$K_a = \frac{[H_3O^+][A^-]}{[HA]} = \frac{[H^+][A^-]}{[HA]}$$

Note: that  $H_2O(l)$  does not go in the dissociation constant.

## Example 7

→ A saturated aqueous solution of benzoic acid,  $C_6H_5COOH$ , has  $pH = 2.93$ . What amount of benzoic acid must have dissolved in order to make 1.00 L of this solution, given that  $K_a = 6.3 \times 10^{-5}$  for benzoic acid?



→ start y x x

**→ Equil  $y-x$**                       x                      x

**→  $x = 10^{-2.93} = 0.0012$**

→  $x^2/(y-x) = 6.3E-5$ ;  $y = 0.023M$ ; get moles

## Determining $K_a$

- Given the equilibrium concentrations, you can determine the  $K_a$  of an acid.
- Given  $K_a$ , you can determine the other parameters in the equilibrium expression.



## Weak bases and $K_b$

→ We can write base dissociation constants for bases just as we did for weak acids.



$$\rightarrow K_b = [BH^+][OH^-]/[B]$$

Some shortcut calculations that were derived from the definitions of weak acids and bases.

→ For weak acids:

$$[\text{H}_3\text{O}^+] = \sqrt{[\text{HA}] K_a}$$
$$\text{pH} = -\log \sqrt{[\text{HA}] K_a}$$

→ Valid when  $[\text{HA}]/K_a > 10^3$ . This means that the relative error will be 1.6%. So, when  $[\text{HA}]/K_a > 10^3$ , can use this equation.

## Example pH, treat as just another equilibrium problem.

→ Need equilibrium, let  $X = [\text{H}_3\text{O}^+]$

→  $\text{HOAc}(\text{aq}) + \text{H}_2\text{O}(\text{l}) = \text{OAc}^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$

→  $K_a = [\text{OAc}^-][\text{H}_3\text{O}^+]/[\text{HOAc}] = 1.8\text{E}-5$

→  $\text{HOAc} + \text{H}_2\text{O} = \text{OAc}^- + \text{H}_3\text{O}^+$

→ Initial	0.1 M		1E-7
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→ Change	-x	x	x
----------	----	---	---

→ Equil	0.1-x	x	x+1E-7
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→ Use that table!!!!!!!!!!!!!!!!!!!!!!

## pH determination

→  $K_a = [x][x + 1E-7]/[0.1 - x] = 1.8E-5$

→ Notice that  $1E-7$  is  $\ll x$  and can neglect.

→  $K_a = [x][x]/[0.1 - x] = 1.8E-5$

→  $x = 1.34E-3$

$$pH \approx -\log \sqrt{[WA] * K_a}$$

→  $pH = -\log[1.34E-3] = 2.87$

→ Please understand on how to solve these equations.

## pHs of salt solutions

- Having the salt of a weak acid will give a basic solution.
- Having the salt of a weak base will give an acidic solution.
- Salts of strong acids and bases will give a neutral  $\text{pH} = 7$  solution.

## Five Titration Cases

- **Case 1: strong acid with strong base**
  - ★ pH = 7 at equivalence point
- **Case 2: weak acid with strong base**
  - ★ pH > 7 (basic) at equivalence point.
- **Case 3: weak base with a strong acid**
  - ★ pH < 7 (acidic) at equivalence point.
- **Case 4: weak base with a weak acid**
  - ★ pH depends on the titrants, not often done.
- **Case 5: weak polyprotic acid with strong base**
  - ★ pH depends on the  $pK_a$ 's of the polyprotic acid.

## Problem 17

- A 100.0 mL sample of 0.20 M  $(\text{CH}_3)_3\text{N}(\text{aq})$ , for which  $K_b = 5.3\text{E}-5$ , is titrated with 0.20 M  $\text{HCl}(\text{aq})$ . Calculate the pH at the equivalence point. Know that SA with WB will give  $\text{pH} < 7$  qualitatively.
- $(\text{CH}_3)_3\text{N}(\text{aq}) + \text{H}_3\text{O}^+(\text{aq}) = (\text{CH}_3)_3\text{NH}^+(\text{aq}) + \text{H}_2\text{O}(\text{l})$
- Need 100 mL of acid to neutralize the base of  $100 \text{ mL} \times 0.2 \text{ mm/mL} = 20 \text{ mm Base}$ .
- Now you made the conjugate acid and its concentration is:
- $0.2 \text{ mm}/(100 \text{ mL} + 100 \text{ mL}) = 0.1\text{M}$  (concentration at equivalence point)

## 17 continued

→ Now hydrolysis reaction:

→ Let  $x = [\text{H}_3\text{O}^+]$

→  $(\text{CH}_3)_3\text{NH}^+(\text{aq}) + \text{H}_2\text{O}(\text{l}) = (\text{CH}_3)_3\text{N}(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$

→ Initial .1 1E-7

→ Change -x x x

→ Equil. .1-x x x+1E-7

→ Since an acid:

→  $K_a = K_w/K_b = 1\text{E-}14/5.3\text{E-}5 = 1.9\text{E-}10$

→  $1.9\text{E-}10 = x^2/(.1-x); x = 4.6\text{E-}6; \text{pH} = 5.36$



# Chapter 19 Ionic Equilibria in Aqueous Systems

## Key Points on Buffered Solutions

- 1. They are weak acids or bases containing a common ion.
- 2. After addition of strong acid or base, deal with stoichiometry first, then equilibrium.

# Henderson-Hasselbach

→ Generalizing:

→  $\text{pH} = \text{pK}_a + \log [\text{CB or SWA}]/[\text{WA}]$  known as Henderson-Hasselbalch equation.

→ Generalizing:

→  $\text{pOH} = \text{pK}_b + \log [\text{CA or SWB}]/[\text{WB}]$  known as Henderson-Hasselbalch equation.

## Making acid buffer

→ Equation is valid when the ratio of the CB to WA varies between 0.10 and 10 and when the concentrations of CB and WA exceed  $K_a$  by a factor of 100. This means that the useful buffer range of a buffer is  $pK_a \pm 1.00$ . For example, HOAc and NaOAc buffer can be made to work between 3.74 and 5.74 ( $pK_a$  of HOAc is 4.74). You will need table of  $pK_a$ 's to design your buffer.

## Making basic buffer

- Equation is valid when the ratio of the CA to WB varies between 0.10 and 10 and when the concentrations of CA and WB exceed  $K_b$  by a factor of 100. This means that the useful buffer range of a buffer is  $pK_b \pm 1.00$ . For example,  $NH_3$  and  $NH_4Cl$  buffer can be made to work between
- $14 - 3.74 = 10.26$  and  $14 - 5.74 = 8.26$  ( $pK_b$  of  $NH_3$  is 4.74). You will need table of  $pK_b$ 's to design your buffer.

# Salts

- When to use  $K_a$  or  $K_b$  for salts:
- Use  $K_a$  when you have the salt of a weak base i.e. conjugate acid (**cation, + charge**) and it hydrolyzes in water.
  - ★  $\text{NH}_4^+(\text{aq}) + \text{H}_2\text{O}(\text{l}) = \text{NH}_3(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$
- Use  $K_b$  when you have the salt of a weak acid i.e. conjugate base (**anion, - charge**) and it hydrolyzes in water.
  - ★  $\text{OAc}^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) = \text{HOAc}(\text{aq}) + \text{OH}^-(\text{aq})$

## Example 8

- Arrange the following 0.10 M aqueous solutions at 25° C in order of increasing pH i.e. getting more basic, given that  $K_a$  for  $\text{CH}_3\text{COOH}$  is  $1.8 \times 10^{-5}$  and that  $K_b$  for  $\text{NH}_3$  is  $1.8 \times 10^{-5}$ .
- A.  $\text{NH}_4\text{Br}$ ,  $\text{CH}_3\text{COOH}$ ,  $\text{CH}_3\text{COONa}$ ,  $\text{NH}_3$
- B.  $\text{NH}_4\text{Br}$ ,  $\text{CH}_3\text{COOH}$ ,  $\text{NH}_3$ ,  $\text{CH}_3\text{COONa}$
- C.  $\text{CH}_3\text{COOH}$ ,  $\text{NH}_4\text{Br}$ ,  $\text{NH}_3$ ,  $\text{CH}_3\text{COONa}$
- D.  $\text{CH}_3\text{COOH}$ ,  $\text{NH}_3$ ,  $\text{NH}_4\text{Br}$ ,  $\text{CH}_3\text{COONa}$
- E.  $\text{CH}_3\text{COOH}$ ,  $\text{NH}_4\text{Br}$ ,  $\text{CH}_3\text{COONa}$ ,  $\text{NH}_3$

## Example 8 Continued

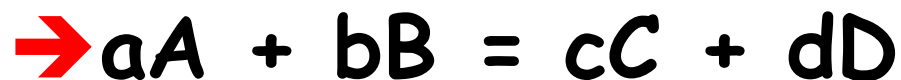
- $\text{NH}_4\text{Br}$ ; acidic  $K_a = K_w/K_b = 5.6\text{E-}10$
- $\text{NH}_3$ ; basic  $K_b = 1.8\text{E-}5$
- $\text{CH}_3\text{COONa}$ ; basic;  $K_b = K_w/K_a = 5.6\text{E-}10$
- $\text{CH}_3\text{COOH}$ ; acidic;  $K_a = 1.8\text{E-}5$
- Increasing pH means higher pH numbers or going to basic. This means lower  $K_a$  to larger  $K_b$ .
- E.  $\text{CH}_3\text{COOH}$ ,  $\text{NH}_4\text{Br}$ ,  $\text{CH}_3\text{COONa}$ ,  $\text{NH}_3$



## Example 9

- What mass of  $\text{Ba}(\text{OH})_2$  must be dissolved in enough water to make a total of 400 mL of solution with  $\text{pH} = 12.15$ ?
- $[\text{H}_3\text{O}^+] = 10^{-12.15} = 7.1\text{E}-3\text{M}$
- $[\text{OH}^-] = 1\text{E}-14 / 7.1\text{E}-3\text{M} = 1.4\text{E}-2\text{M}$
- $1.4\text{E}-4\text{M}$  (1mol  $\text{Ba}(\text{OH})_2$  / 2 mol  $\text{OH}^-$ )  
(171.3 g/mol)(0.4L) = 0.48 g

## Writing $K_{sp}$



→ Again, balance equation very important.

$$K_{eq} = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

→ Call this  $K_{sp}$

## Solubility



→  $K_{\text{sp}} = [\text{Mg}^{2+}]^3 [\text{PO}_4^{3-}]^2 = 1\text{E}-25$

→ Let  $x$  = solubility of  $\text{Mg}_3(\text{PO}_4)_2$



→ Initial	$x$	0	0
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→ Change	$-x$	$3x$	$2x$
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→ Equil	0	$3x$	$2x$
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→  $K_{\text{sp}} = [3x]^3 [2x]^2; x = 3.92\text{E}-6 \text{ moles/l}$

## Chapter 20.1

→ Second law of thermodynamics deals with entropy (disorder). Know the different states of matter and the entropy change for the universe  $> 0$  for a spontaneous process.

# The Second Law of Thermodynamics

→ . . . in any spontaneous process there is always an increase in the entropy of the universe.

$$\rightarrow \Delta S_{\text{univ}} > 0$$

★ for a spontaneous process.

1877 Ludwig Boltzman

$$S = k \ln W$$

where  $S$  is entropy,  $W$  is the number of ways of arranging the components of a system, and  $k$  is a constant (the Boltzman constant),  $R/N_A$  ( $R$  = universal gas constant,  $N_A$  = Avogadro's number).

- A system with relatively few equivalent ways to arrange its components (smaller  $W$ ) has relatively less disorder and low entropy.
- A system with many equivalent ways to arrange its components (larger  $W$ ) has relatively more disorder and high entropy.

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0$$

*This is the **second law of thermodynamics**.*

# Calculating the change in entropy of reaction?

- Need to predict and calculate change in entropy as a reaction proceeds.
- Such calculations are needed to understand reactions both simple and complex.
- Lets use Hess's law to define the change in entropy during a reaction.

$$\Delta S_{\text{rxn}}^0 = \sum m S_{\text{products}}^0 - \sum n S_{\text{reactants}}^0$$

- Where m and n are the mole amounts from the balanced equation.

## Entropy Changes in the System

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$\Delta S^0_{\text{rxn}}$  - the entropy change that occurs when all reactants and products are in their standard states.

$$\Delta S^0_{\text{rxn}} = \sum \Delta S^0_{\text{products}} - \sum \Delta S^0_{\text{reactants}}$$

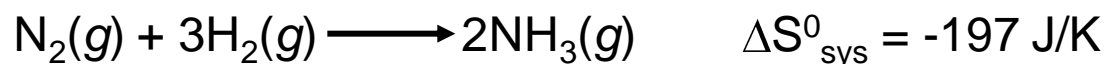
The change in entropy of the surroundings is directly related to an opposite change in the heat of the system and inversely related to the temperature at which the heat is transferred.

$$\Delta S_{\text{surroundings}} = - \frac{\Delta H_{\text{system}}}{T}$$



## Sample Problem 20.3      Determining Reaction Spontaneity

**PROBLEM:** At 298K, the formation of ammonia has a negative  $\Delta S^0_{\text{sys}}$ :



Calculate  $\Delta S^0_{\text{rxn}}$ , and state whether the reaction occurs spontaneously at this temperature.

**PLAN:**  $\Delta S^0_{\text{universe}}$  must be  $> 0$  in order for this reaction to be spontaneous, so  $\Delta S^0_{\text{surroundings}}$  must be  $> 197 \text{ J/K}$ . To find  $\Delta S^0_{\text{surr}}$ , first find  $\Delta H_{\text{sys}}$ ;  $\Delta H_{\text{sys}} = \Delta H_{\text{rxn}}$  which can be calculated using  $\Delta H^0_{\text{f}}$  values from tables.  $\Delta S^0_{\text{universe}} = \Delta S^0_{\text{surr}} + \Delta S^0_{\text{sys}}$ .

**SOLUTION:**  $\Delta H^0_{\text{rx}} = [(2 \text{ mol})(\Delta H^0_{\text{f}}\text{NH}_3)] - [(1 \text{ mol})(\Delta H^0_{\text{f}}\text{N}_2) + (3 \text{ mol})(\Delta H^0_{\text{f}}\text{H}_2)]$

$$\Delta H^0_{\text{rx}} = -91.8 \text{ kJ}$$

$$\Delta S^0_{\text{surr}} = -\Delta H^0_{\text{sys}}/T = -(-91.8 \times 10^3 \text{ J}/298 \text{ K}) = 308 \text{ J/K}$$

$$\Delta S^0_{\text{universe}} = \Delta S^0_{\text{surr}} + \Delta S^0_{\text{sys}} = 308 \text{ J/K} + (-197 \text{ J/K}) = 111 \text{ J/K}$$

$\Delta S^0_{\text{universe}} > 0$  so the reaction is spontaneous.

## Sample Problem 20.2     Calculating the Standard Entropy of Reaction, $\Delta S^{\circ}_{\text{rxn}}$

**PROBLEM:** Calculate  $\Delta S^{\circ}_{\text{rxn}}$  for the combustion of 1 mol of propane at 25°C.



**PLAN:** Use summation equations. It is obvious that entropy is being lost because the reaction goes from 6 mols of gas to 3 mols of gas.

**SOLUTION:** Find standard entropy values in the Appendix or other table.

$$\Delta S = [(3 \text{ mol})(S^{\circ} \text{CO}_2) + (4 \text{ mol})(S^{\circ} \text{H}_2\text{O})] - [(1 \text{ mol})(S^{\circ} \text{C}_3\text{H}_8) + (5 \text{ mol})(S^{\circ} \text{O}_2)]$$

$$\Delta S = [(3 \text{ mol})(213.7\text{J/mol}\cdot\text{K}) + (4 \text{ mol})(69.9\text{J/mol}\cdot\text{K})] - [(1 \text{ mol})(269.9\text{J/mol}\cdot\text{K}) + (5 \text{ mol})(205.0\text{J/mol}\cdot\text{K})]$$

$$\Delta S = - 374 \text{ J/K}$$

Careful of units!

# Exam Preparation

- Don't stay up all night,
- Eat a good meal,
- Check the batteries in your calculator,
- Arrive early to exam to relax,
- Don't panic in exam,
- Look at one problem at a time,
- Check your work,
- You will do great!!!!!!!!!!